THE PROPERTIES OF SOME COPPER ALLOYS.

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DURING the past four years the Metallurgy Department of the National Physical Laboratory has been called upon to prepare a series of alloys of copper designed to meet certain special requirements. In the case of one group of these alloys it was considered desirable to avoid the use of zinc, while in the second group it was considered essential to avoid the use of aluminium or a high percentage of zinc. A considerable number of alloys have been prepared and rolled, and mechanical tests have been carried out upon them. Although the circumstances in which this work was carried out did not permit of a systematic investigation of the various alloy systems concerned, so that it cannot be claimed that the alloys described below are the best of their respective series, the data obtained in connection with them appear to be of sufficient interest to warrant publication. The present account of these alloys is therefore given for the purpose of placing at the disposal of workers in non-ferrous metals the compositions and mechanical properties of these materials, and of describing some of the difficulties met with in the preparation of these alloys, and the methods which have been adopted to overcome them.

It should be pointed out that the requirements which these alloys were intended to meet are of a very severe character, involving extensive cold working, so that the alloys had to be capable of being rolled into thin sheet, which was required to have an excellent finish and to undergo further operations without cracking. A combination of high tensile strength with great ductility was therefore aimed at in every case.

The materials used throughout the work described in this paper consisted of electrolytic copper, high-grade aluminium (containing approximately 99·5 per cent. aluminium), and cupro-manganese (containing 30 per cent. manganese). The zinc employed was a high-grade material of American origin, an analysis of which showed the following results :—

						Per cent.
Iron	..	..	..	..	..	..	0·0175
Copper	..	..	..	..	..	..	0·006
Lead	..	..	..	..	..	..	traces
Cadmium	..	..	..	..	..	..	traces

Nickel was used in the form of shot made by the Mond process.

SECTION I.—ALLOYS OF COPPER WITH ALUMINIUM, WITH MANGANESE, AND WITH MANGANESE AND ALUMINIUM, NOT CONTAINING ZINC.

Melting of the Alloys.—The copper was first melted down in a 60-lb. Salamander crucible under a layer of charcoal. As soon as this was molten the manganese was added in the form of cupro-manganese, and the temperature of the furnace was maintained until this was completely dissolved. The contents of the crucible were then well stirred and the aluminium added in the form of solid pure metal, the molten alloy being well stirred at the same time to ensure complete mixing. In some cases, where the amount of aluminium to be added was not large, an addition was made after the pot had been removed from the furnace and immediately before casting. There was, as usual, a marked rise of temperature on the addition of the aluminium. Before casting, the metal was carefully stirred with a graphite rod, the sides of the crucible being scraped to remove as much adhering dross and charcoal as possible. The metal was finally skimmed with great care with an iron skimmer coated with a wash of ganister in order to protect it from solution in the metal.

Casting.—The first method tried was that of casting the metal in the ordinary way by pouring it into preheated cast-iron moulds which had previously been dressed with black-lead paste. Even when the greatest care was taken in the casting process, and every endeavour was used to prevent the entrance of dross and small particles of charcoal into the mould, it was found difficult to obtain ingots with surfaces which could be regarded as satisfactory for the purpose in question. Slabs could be obtained which were quite sound and free from blowholes, but small particles of dross were frequently entangled in the surface, causing small imperfections which gave rise to slight spills and defects in the finished strip or sheet. As these interfered seriously with the desired uses of the sheet, it became necessary to avoid their occurrence.

A flux, consisting of cryolite, added after the metal had been taken out of the furnace, was tried. This proved partially successful, but even with its use it was not possible to secure perfect ingots with certainty and regularity. Another method was then tried.

Pressure Casting.—The defects noted above arose from the presence of foreign matter floating on the surface of the molten metal, and, in spite of every care, finding its way in small quantities into the mould. The obvious remedy seemed to be to cast the metal by tapping it from a point well below the surface, and the most satisfactory method of accomplishing this appeared to be a process sometimes known as " pressure casting," which has been developed and patented by Mr. F. Tomlinson of the Broughton Copper Company, Ltd., Manchester. An adaptation of that method has been used with considerable success for dealing with these alloys. The principle of the method consists in forcing the liquid metal, by means of externally applied air pressure, through a feeder-tube communicating with the bottom of the mould and dipping into the molten metal nearly to the bottom of the crucible.

In order to carry this out it is necessary to use a previously heated feeder-tube, through which the metal can be forced without splashing and without exposure to the atmosphere, the dross, charcoal, &c., being left behind in the crucible. The amount of metal in the crucible must be so adjusted that the mould is filled before the bottom of the feeder-tube is exposed, and the air pressure on the metal must be maintained until the ingot has become solid.

The apparatus used is illustrated diagrammatically in fig. 1. A is a cylindrical cast-iron vessel closed at the bottom, while the upper end is open and has an external flange. The crucible, C, stands on a fireclay support, P. The top of the cast-iron vessel, A, is closed by means of a lid, B, which is provided with an annular recess, R, fitted with an asbestos washer for the purpose of making an air-tight joint with the top of the vessel, A, to which it can be tightly clamped by means of a number of screw clamps (not shown in the diagram). The centre of the lid is provided with a hole, 3 inches in diameter, into which fits a circular flange piece of steel, E, which is screwed to the iron tube, D, $\frac{3}{4}$-inch in internal diameter. This is the feeder-tube, and its length is so arranged that it reaches nearly to the bottom of the crucible, C. The steel piece, E, is separated from the lid by another asbestos washer, the object being to form an air-tight joint and also to reduce the loss of heat from the tube, D, to the cold lid of the vessel. The feeder-tube and its holder are held in position by the clamping-bar, G, which consists of a flat strip of steel slotted in the centre to take the top of the tube, and near the ends to enter corresponding slots in studs, HH. The clamping is performed by slipping the centre slot over the projection of the tube, and springing the plate until it is possible to engage the end slots in studs, HH. The " spring " of this strip, together with the weight of the mould, is sufficient to hold the tube in place against the internal pressure in the vessel A. A two-part mould, L, fitted with a hole in the bottom, fits over the projecting part of the tube, D. The pressure vessel, A, is connected with a compressed air main through the inlet, M, the supply being regulated by means of a delicate needle-valve ; an exhaust valve, N, is also fitted. A pressure gauge, S, is provided.
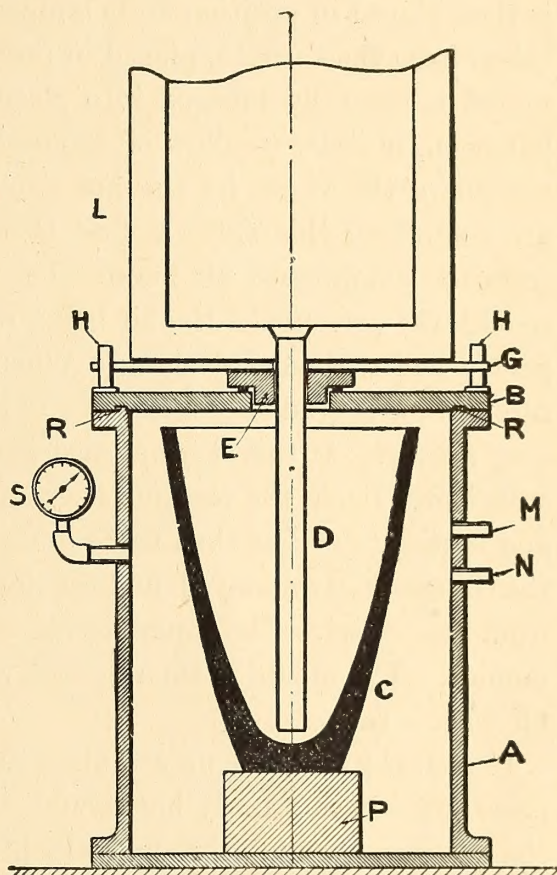

Fig. 1.

Casting Operation.—The requisite amount of metal is melted in the manner described above, except that it has been found convenient to add the aluminium while the crucible

is still in the furnace ; this is done because it was found necessary, for this method of casting, to work at somewhat higher temperatures. When the last addition has been made the crucible is moved to one side of the furnace, and the feeder-tube with its steel flange screwed in position is inserted into the furnace and left there until it has reached a bright red heat. The pot is then removed from the furnace, rapidly skimmed free from most of the charcoal, and a little cryolite is thrown on to the surface. The crucible is then placed in the pressure vessel, the surface of the metal being again skimmed to leave the centre portion as clean as possible for the entrance of the feeder-tube. The lid is then placed in position and clamped on. While this is being done the runner-tube is taken from the furnace, placed in position and clamped. Then the previously prepared mould is carefully lowered into place. During these operations the exit valve, N, is left open, in order to allow of the escape of the expanding air caused by the heating of the air in the vessel by the hot crucible, feeder-tube, &c. As soon as the operations are completed this valve is first closed and then air is slowly admitted to the vessel from the compressed air main. The metal rises in the feeder-tube and flows into the mould, the pressure of the air being regulated in such a manner that the mould is filled gently and without splashing. When the metal approaches the top of the mould the rate of flow is gradually reduced and is almost arrested, the last stages being carried out very slowly. At this stage a crust is formed on the top of the ingot. As soon as this is sufficiently thick, the pressure is gradually raised in the vessel to 30 lb. per square inch, and is maintained at that value until the ingot is solid. The pressure is then released, the clamping bar removed, and the ingot mould with the feeder-tube attached is removed from the vessel. The liquid residue in the crucible can then be cast into small ingot moulds. The mould is then opened and the runner removed from the ingot by cutting off with a saw.

If suitable precautions are observed this process is eminently satisfactory, but it is necessary to use a fairly hot mould, since, otherwise, the metal is liable to be chilled in the narrow opening through which it has to pass before the mould can be filled. Conditions should be so arranged that this orifice in the bottom of the mould remains open until the whole of the ingot is solidified. In the present experiments the mould was preheated in a special gas furnace in such a manner that the bottom of the mould was distinctly hotter than the top. The actual mould temperatures were of the order of 500° C. to 600° C. at the bottom.

It was found that as a rule a slight amount of shrinkage occurred at the top surface of the ingot ; this suggests that setting did not actually commence at the top but at some point lower down. A slight amount of cropping was therefore necessary. Attempts were made to eliminate this by closing the top of the mould and forcing the metal up into contact with it. This gave an ingot of good external appearance, but there were signs that slight internal cavities had been formed. Such a defect is liable to give longitudinal unsoundness in the finished strip, and this device was therefore abandoned.

Used in the manner indicated this method of casting has given very successful results, all surface defects of any kind being entirely eliminated. The size of the slabs produced was 14 inches × 7 inches × 1½ inches.

The composition of the alloys cast in this manner, together with the results of mechanical tests, are given in Table I. Before considering this table in detail, however, it may be well to mention a point in connection with the casting of manganese-copper alloys. Difficulty has been experienced with these on account of the readiness with which the surface becomes oxidized. Even during the short interval necessary for casting the alloy becomes covered with a thick black coating of oxide, which is liable completely to ruin the surface of the ingot. It has been found that the addition of 0·25 per cent. of aluminium prevents this oxidation and removes this defect entirely.

Rolling of the Alloys.—The rolling of these alloys has presented no difficulty whatever. They were broken down hot (temperature about 800° C.) from a thickness of 1½ inches to about ⅜-inch. The strips thus produced were pickled and then cold rolled to a thickness of 0·14-inch. Some of the strips thus produced have subsequently been annealed and further cold rolled to a thickness of 0·04-inch. The annealing of these alloys for the purpose of further cold rolling can be conveniently carried out at any temperature between 500° C. and 800° C. A range of from 650° C. to 750° C. is convenient and satisfactory.

The alloys which contain manganese tend to become oxidized on the surface during annealing, and this oxide is somewhat adherent and difficult to remove. The pickling appears to be best done by dipping the alloy, while still hot, into hydrochloric acid of specific gravity 1·1.

The results of tensile and Brinell tests on these alloys in the form of strip 0·14-inch thick are given in Table I. The Brinell tests, in view of the thin section of material available, have been made with a ball 5 mm. diameter and a load of 300 kg. Under these conditions the impressions are not very deep, but the results must be taken with the reservation which necessarily applies to Brinell tests on such thin material.

The results shown in Table I. are remarkable for the very high degree of ductility which can be obtained, together with considerable tensile strength, by the use of aluminium or aluminium plus manganese. Probably the most remarkable result is that for the alloy No. 3 containing 7 per cent. aluminium without manganese, which in the " as rolled " condition attains a tensile strength only just under 40 tons per square inch, with an elongation of 17·5 per cent., while the same alloy after annealing still has a tensile strength of 27·5 tons per square inch and the remarkable elongation of 71 per cent. The results for this alloy are closely approached by the alloy No. 6 containing 7 per cent. aluminium and 1 per cent. manganese, where the figures are 35·5 tons per square inch tensile strength, with 28 per cent. elongation in the " as rolled " condition, and 29·3 tons per square inch tensile strength, with 65 per cent. elongation in the annealed condition. Similarly remarkable results are given by the alloy (No. 8) containing 6 per cent. aluminium and 3 per cent. manganese. The results

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TABLE I.—Alloys of Copper with Aluminium and Manganese.

No.	Chemical composition.		Condition of alloy.	Yield stress.	Ultimate stress.	Elongation.	Brinell number.
	Aluminium.	Manganese.		Tons per sq. in.	Tons per sq. in.	Per cent. on 2⅜ in.	
	Per cent.	Per cent.					
1	3	0	As rolled	26·6	26·8	9	137·5
			Annealed*	5·8	17·7	55	60
2	5	0	As rolled	34·3	35·1	16·5	174·5
			Annealed*	8·3	25·5	70	84·5
3	7	0	As rolled	38·7	39·8	17·5	195
			Annealed*	7·0	27·5	71	75·5
4	3	1	As rolled	26·2	26·8	11·5	141·5
			Annealed*	10·0	20·2	50	72·5
5	5	1	As rolled	28·7	31·1	27	162·5
			Annealed*	12·0	26·3	57	89·5
6	7	1	As rolled	34·1	35·5	28	184
			Annealed*	11·5	29·3	65	99·5
7	3	3	As rolled	27·3	27·7	12	140
			Annealed*	10·2	21·4	48	78·5
8	6	3	As rolled	38·2	39·0	12	—
			Annealed*	13·7	29·8	58	—
9	2	5	As rolled	29·6	29·9	9	145
			Annealed*	10·4	22·4	45	83
10	4	5	As rolled	35·0	35·7	15·5	182
			Annealed*	11·3	26·7	55	95
11	0	5	As rolled	29·3	29·3	9	149·5
			Annealed*	9·2	21·0	45	81
12	0	7	As rolled	29·4	29·4	8·5	182
			Annealed*	10·6	22·1	44	95

The figures given in the above table are mean values obtained from two test-pieces from each alloy. In no case was there any noteworthy disagreement between duplicate tests.

for the last two alloys in the table (Nos. 11 and 12) containing no aluminium are also interesting, although the figures are distinctly lower than for the alloys in which aluminium is present.

Microstructure.—In the annealed state all the alloys described in Table I. consist of homogeneous solid solution. The chief point of interest with regard to their structure is illustrated in figs. 2 and 3 (Plate 1), under a magnification of 150 diameters. These photomicrographs show the effect of manganese in restraining crystal growth during annealing. The alloy represented by fig. 2 (No. 3) contains 7 per cent. aluminium, while that of fig. 3 contains 7 per cent. aluminium plus 1 per cent. manganese (No. 6). After similar mechanical treatment both have been annealed for thirty minutes at 650° C. It will be seen that the crystal size attained by the alloy (No. 6) containing

* The annealed test-pieces were heated at 650° C. for half an hour and cooled in air.

Fig. 2.—Alloy of copper containing 7 per cent. of aluminium—cold rolled and annealed at 650° C. for 30 minutes. Magnified 150 diameters. Etched with copper ammonium chloride.

Fig. 3.—Alloy of copper containing 7 per cent. of aluminium and 1 per cent. of manganese—cold rolled and annealed at 650° C. for 30 minutes. Magnified 150 diameters. Etched with copper ammonium chloride.
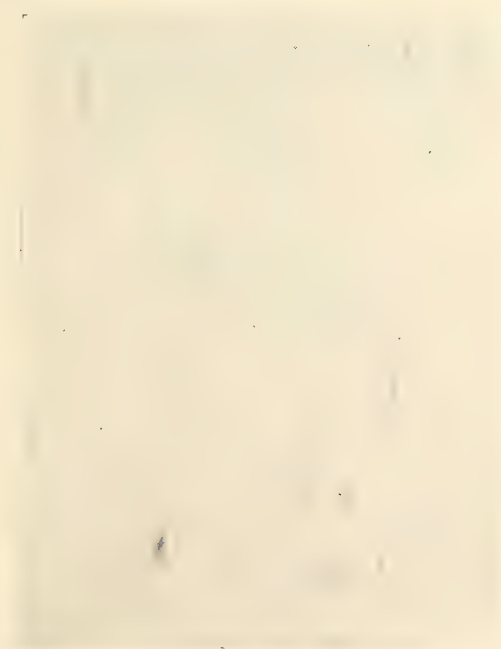

Fig. 4.—Alloy of copper containing 5 per cent. of manganese and 1 per cent. of lead—as rolled. Unetched. Magnified 150 diameters.

manganese is very markedly smaller than that of the other alloy. It may be interesting to mention in this connection that similar observations as to the effect of manganese on rate of crystal growth have been made in a light alloy of aluminium containing zinc and copper, which has been studied by one of the present authors and Mr. S. L. Archbutt.

Section II.—Alloys Free from Aluminium.

The alloys of this group have been investigated at a different time from those described above. The conditions to be met with in this group required that no aluminium should be used in their manufacture, while the alloys themselves were required to withstand severe stamping and drawing operations in the form of thin strip less than $\frac{1}{20}$th of an inch thick. In the production of these alloys different casting methods have been adopted, and very much smaller ingots, 12 inches $\times$ 5 inches $\times$ 0·75-inch thick, weighing about 15 lb., have been used.

The pressure casting method described in connection with the previous group of alloys was not adopted because, in the first intance, alloys not described in the present paper were experimented with, whose very high melting-point made the use of an iron feeder-tube impracticable. Subsequently, the methods of casting evolved for these high melting-point alloys were adapted and found satisfactory for the materials described below.

It was found at the outset that it was difficult to obtain, from metal melted under charcoal, ingots perfectly free from defects, however carefully the skimming operation was carried out before pouring. Particles of dross and charcoal could not be entirely eliminated, and gave slight surface defects, traces of which could be found on the finished strip. The addition of a little borax as well as charcoal was tried, with the object of preventing the formation of dross, but it was found impossible to skim the alloy quite free from borax, and some entered the mould, carrying a certain amount of charcoal with it. This spoiled the surface of the ingot.

Finally the alloys were prepared with the aid of borax alone. This was added with the first charge, and consequently melted before the alloy. The metal as it melts then runs to the bottom of the crucible and immediately becomes covered with a film of borax, which not only protects it from oxidation but dissolves any free oxide which is present. When the alloy is completely molten it is removed from the furnace and skimmed as well as possible before pouring. While the whole of the borax could not be completely removed from the surface of the molten metal, only a little entered the mould when the alloy was poured, and it was found that the borax, being much lighter than the alloy, floated to the surface of the metal in the mould, until the rising metal pressed the globular borax against the side of the mould, in which position it became fixed. As the borax in these circumstances is still fluid it becomes considerably flattened by the pressure of the metal, and on removing the alloy from the mould it was found that the borax fell away, leaving merely shallow depressions on the surface.

On rolling, these slight depressions disappear completely during the first few passes, and are therefore without effect on the metal in its later stages.

By this method the alloys, particulars of which are given in Table II., were, among others, successfully cast into sound ingots which were subsequently rolled into strips free from surface defects of any kind.

Rolling of the Alloys.—The alloys were cold rolled from the cast slab down to a thickness of 0·04-inch in the experimental rolling-mill at the National Physical Laboratory. All the alloys rolled with ease, and with one intermediate annealing at a thickness of either 0·375-inch or 0·15-inch gave strip free from edge-cracking. Some of the alloys were rolled cold from a thickness of 0·75-inch to 0·04-inch, but edge-cracking appeared to a slight extent in the later stages. The most satisfactory strip was obtained by cold rolling from a thickness of 0·75-inch to 0·15-inch, annealing at a temperature of 650° C., and finishing cold to a thickness of 0·04-inch.

The results of mechanical tests on a number of these alloys are given in Table II.

TABLE II.—Alloys containing no Aluminium.

No.	Chemical composition.					Condition of alloy.	Yield stress. Tons per sq. in.	Ultimate stress. Tons per sq. in.	Elonga-tion. Per cent. on 2 in.	Remarks.
	Cu.	Mn.	Zn.	Ni.	Pb.					
13	95·5	4	—	—	0·5	As rolled / Annealed*	30 (?) / 11	38 / 21	4·5 / 35	Yield points indefinite. Strip very laminated.
14	88	2	10	—	—	As rolled / Annealed*	35 / 8	37 / 21	5 / 41·5	
15	87	3	10	—	—	As rolled / Annealed*	42 / 11	47 / 23	3 / 35	Yield points indefinite.
16	85	—	5	10	—	As rolled / Annealed*	31 / 8	34 / 20	— / —	Broke outside gauge marks.
17	88	—	7	5	—	As rolled / Annealed*	27·5 / 7	32·5 / 19	— / 40·5	Broke outside gauge marks.
18	80	—	10	10	—	As rolled / Annealed*	35 (?) / 10	39 / 21	3 / 35	Yield points indefinite.

In addition to the tests described in the above table, a considerable number of other alloys were also submitted to a severe form of cupping test, and, with the exception of the alloy (No. 13) containing 4 per cent. manganese and 0·5 per cent. lead, were found satisfactory. The latter alloy (the first one of this table) is extremely laminated in the form of strip and is quite unsuitable for drawing and cupping operations.

A number of other alloys, in addition to those mentioned in Table II., were also cast and rolled, but after certain special tests had been carried out on them no material

* Annealing was carried out at 650° C. for thirty minutes.

remained for tensile tests, which cannot therefore be given at the present time. The alloys thus prepared included those shown in Table III.

TABLE III.

Manganese per cent.	Aluminium per cent.	Zinc per cent.	Lead per cent.
5	—	—	1
3	—	10	1
3	—	5	—
—	3	10	—
—	3	10	1

The introduction of lead into some of these alloys was tried with a specific object, but they were found to be very laminated. The lead appears to occur in the free state in the metal in the form of long strings of small globules. This structure is illustrated in fig. 4 (Plate 1) under a magnification of 150 diameters. This figure represents an alloy containing 5 per cent. manganese and 1 per cent. of lead. The specimen has been photographed without etching.

A comparison of Table II. with Table I. shows that the alloys have in no case such remarkable properties as those which have been referred to in connection with Table I., but attention may be drawn to the alloy (No. 15) containing 3 per cent. manganese and 10 per cent. zinc, which, in the cold rolled condition, has a tensile strength of 47 tons per square inch, with 3 per cent. elongation, and in the annealed condition a tensile strength of 23 tons per square inch, with 35 per cent. elongation.